Presented at the Materials Research Society
Annual Meeting, Boston, November 1-4, 1982

ENHANCED ADHESION FROM HIGH ENERGY ION IRRADIATION*

B. T. WERNER, T. VREELAND, Jr.†, M. H. MENDENHALL,

Y. QIU, and T. A. TOMBRELLO

W. K. Kellogg Radiation Laboratory
California Institute of Technology, Pasadena, California 91125

ABSTRACT

We have found that irradiation of a variety of thin film substrate combinations by MeV/amu heavy ion beams will produce a remarkable enhancement in the adherence of the film. For example, gold films can be firmly attached to soft materials like teflon using a 1 MeV beam of protons (10^{14} cm^{-2}) or helium ions (10^{13} cm^{-2}) and to harder materials like silicon (10^{15} cm^{-2}), quartz (2×10^{15} cm^{-2}) and tungsten (2×10^{14} cm^{-2}) with 0.5 MeV/amu beams of fluorine or chlorine ions. In the case of metal films on semiconductors a low resistance contact results. The mixed layer at the interface is observed to be quite thin ($\lesssim$ 50 Å); for Ag on Si electron diffraction and imaging studies of the interface region reveal the presence of crystalline Ag compounds.

---

*Supported in part by the National Aeronautics and Space Administration [NAGW-202 and -148] and the National Science Foundation [PHY79-23638].

†Department of Engineering and Applied Science.

ONE OF THE BAND AID PREPRINT SERIES
IN ATOMIC & APPLIED PHYSICS

October 1982

Introduction

The adhesion enhancement of thin metal films on insulators, semiconductors, and metals by high energy ion bombardment was recently reported by Mendenhall et al.[1] Various combinations of materials have been tested, but none have been found for which the bond is not significantly improved (see Table I). The ion beam energies are chosen to lie near the peak of the cross section for energy loss to electrons by the incident ion ($\sim$ 0.5 MeV/amu) where the nuclear component of the energy loss is negligible. The doses required for good adhesion extend from 10^{13} to 10^{16} ions/cm^2.

This technique was first suggested for use with insulators.[2] A thin mixed layer was predicted to be formed at the interface by the same mechanism by which tracks are produced in insulators with high energy ions. Briefly, tracks are formed at these energies when the excitation of the electrons by the bombarding ion disturbs the interatomic potential.[3,4] This can lead to the transfer of energy to atoms in the lattice and subsequent damage track production. If the relaxation time of the electrons is too fast, as it is believed to be in semiconductors and metals, this will not occur. In fact, tracks have not been observed in these materials; therefore, it does not seem possible to explain the enhanced adhesion with this model. As discussed by Mendenhall et al., Rutherford backscattering profiles have indicated that if a mixed layer is present it is less than $\sim$ 50 Å thick.[1]

The aim of our investigations has been to discover the mechanism for the adhesion enhancement. In this paper we describe a preliminary TEM study of thinned bonded samples of silver on silicon using electron diffraction. The Ag-Si system was chosen because it is expected that the effects of the irradiation will be distinct from other bonding mechanisms; the bonding is poor without irradiation and ion beam mixing in the keV range has so far not

produced any silver-silicon compounds.[5] Several silver-silicon phases have been reported in the literature. An hcp structure, β silver-silicon has been found and confirmed using the splat cooling technique.[6] The composition is 5-25 atomic per cent Si with lattice parameters a = 2.87 Å and c = 4.53 Å. Splat cooling was also used to find a complicated structure containing about 30 atomic per cent Si.[7] The lattice was interpreted as being orthorhombic with a = 5.56 Å, b = 9.16 Å, and c = 8.49 Å. Recently, a metastable crystalline silver silicide was formed by pulsed laser irradiation at a silver-silicon interface.[5] The composition was roughly 14 atomic per cent Si (the eutectic composition), but the structure was not determined.

Sample Preparation

Antimony doped n-Si wafers of both [111] and [100] orientations were etched in HF, washed with methanol and then quickly transferred to the vacuum apparatus for vapor deposition of about 500 Å of Ag at 10^{-6} torr. On some samples, an attempt was made to further clean as well as impede the formation of an oxide layer on the etched surface of the Si; this included rinsing in an acetone-bromine solution and freezing acetone on the Si surface to protect it during pump down. Preventing the formation of less than two monolayers of oxide seems not to be possible without keeping the Si under high vacuum.

The samples were irradiated using the Caltech tandem Van de Graaff accelerator. Most of them were bombarded with ^{35}Cl ions at 20 MeV, receiving doses of 5×10^{15} ions/cm^2 (good adhesion enhancement) or 1×10^{15} ions/cm^2 (minimal adhesion enhancement). A typical flux was about 1.5×10^{12} ions/cm^2 sec. 10 MeV ^{19}F ions were used for some samples, with doses of 3×10^{16} ions/cm^2 and 1×10^{16} ions/cm^2. Most of the beam spots were 2 × 2 mm. After irradiation, scotch tape applied to the silver film removed all but that on the beam spot.

Disks 2.3 mm in diameter were cut out around the beam spots. The disks

were soaked in HNO_3 to remove all or part of the remaining Ag film. With some samples this was unnecessary as the film had been partially or entirely ripped off during the cutting process. They were chemically (jet) thinned from the back (non-irradiated) side using a combination of HNO_3 and HF. CP4 was employed for final thinning of some samples.

Heating to about 100°C was necessary to melt the wax used in mounting the disks for thinning. The wax was removed by TCE and chloroform. The samples were rinsed with acetone, water and methanol at various stages of the preparation process.

Results

The silver-silicon interface was examined using TEM with 100 keV electrons. On three high dose (5×10^{15} ions/cm^2) chlorine ion beam spots (three different Si [111] substrates), a polycrystalline fcc structure with lattice parameter $a = 5.57 \pm 0.07$ Å was observed. We interpret this as being AgO_2 with the NaCl structure (space group O^5_h-Fm3m).[8] Using the metallic Goldschmidt radii for Ag (1.44 Å) and Si (1.32 Å),[9] the calculated lattice parameter for $AgSi_2$ is 5.56 Å, which would also agree well with the measured value. A total of fourteen high dose Cl ion samples have been examined; we believe that the formation of the silver compound is critically dependent on the preparation parameters, as discussed in the next section. This silver compound has not been observed on low dose (1×10^{15} ions/cm^2) or control (non-irradiated) samples, which indicates that it is either beam induced or is a consequence of the better bonding of the Ag to the substrate.

Discussion

Although we have observed isolated instances of crystalline silver compounds in the interface region, these epitaxial phases are probably not the

controlling factor in the general adhesion enhancement mechanism because they do not occur on all the irradiated samples. This is supported by the wide variety of film substrate combinations that have successfully been bonded, which makes a dependence on geometrical matching conditions, etc., unlikely. Our measurement of adhesion has not been more quantitative than the scotch tape test; however, recent observations of the effect of HNO_3 on the Ag films suggest that the adhesion is greatest near to the edge of some beam spots, where the dose and flux are as much as 30% less than at the center. In addition, two of the samples on which Ag compounds were found were irradiated at low flux ($\frac{1}{2}$ to $\frac{1}{4}$ the standard flux). The thin area examined with TEM was near to the center of most beam spots. This could explain why we have seen the material on only three samples. Perhaps high flux irradiation either inhibits its growth or destroys it once it has formed.

The creation of silver compounds and the possible existence of recrystallized grains may imply atomic mobility and hence a mechanism for transferring energy from the electrons to the lattice. One possibility is that the track mechanism operates in the insulating oxide surface layer. This seems to be contradicted by the apparent decrease in adhesion enhancement with increasing oxide layer thickness.[1] The rate of energy deposition at the interface is not large enough to cause significant macroscopic heating of the silicon; thus, the lattice disorder at the interface may be caused by the interaction of the bombarding ions with electrons in surface states, which could behave differently in this situation from electrons in the bulk material.

Acknowledgments

This work was supported in part by the National Aeronautics and Space Administration [NAGW-202 and -148] and the National Science Foundation [PHY79-23638].

References

1. M. H. Mendenhall, Y. Qiu and T. A. Tombrello, submitted to Science, July 1982.
2. J. E. Griffith, Y. Qiu and T. A. Tombrello, Nucl. Instrum. Meth. 198 (1982) 607.
3. T. A. Tombrello, Proc. Int'l. Workshop on Desorption Induced by Electronic Transitions; Williamsburg, VA, May 12-14, 1982 (in press).
4. C. C. Watson and T. A. Tombrello, Proc. Lunar Planet. Sci. Conf. 13th, (1982) 845, and submitted to Rad. Eff. (1982).
5. S. S. Lau, B. Y. Tsaur, M. von Allmen, J. W. Mayer, B. Stritzker, C. W. White and B. Appleton, Nucl. Instrum. Meth. 182/183 (1982) 97.
6. T. R. Anantharaman, H. L. Lou and W. Klement, Jr., Nature, 210 (1966) 1040.
7. C. Suryanarayana, J. Less-Common Metals, 35 (1974) 347.
8. Yu. N. Borisenko and V. T. Gritsyna, Fiz. Khim. Obrab. Mater., No. 6 (1976) 24.
9. R. P. Elliott, Constitution of Binary Alloys, First Supplement, McGraw-Hill, New York, 1965.

TABLE I

MATERIAL AND BEAM COMBINATIONS TESTED

For the cases shown thin layers (~ 500 Å) of the metal were evaporated onto the substrate and then irradiated at low beam current with the ion beams indicated. In all cases the resulting bond passed a Scotch Tape test; in many cases the metal could only be removed by scraping. For the semiconducting substrates (Si, InP, GaAs) the result was a low resistance ohmic contact.

MATERIAL	BEAM, MINIMUM DOSE/cm^2
Au on Teflon	1.5 MeV ^4He, 1×10^{13}
	1 MeV ^1H, 1×10^{14}
Au on SiO_2	20 MeV Cl, 2×10^{15}
Ag on SiO_2	20 MeV Cl, 2×10^{15}
Au on CaF_2	20 MeV Cl, 2×10^{14}
Au on Ferrite	20 MeV Cl, 3×10^{13}
	5 MeV F, 2×10^{15}
Au on Al_2O_3	20 MeV Cl, 5×10^{15}
Pd on Al_2O_3	20 MeV Cl, 2×10^{15}
Au on Si	20 MeV Cl, 1×10^{15}
Ag on Si	20 MeV Cl, 5×10^{15}
	10 MeV F, 1×10^{16}
Au on InP	20 MeV Cl, 5×10^{14}
Ag on InP	20 MeV Cl, 5×10^{14}
Au on GaAs	20 MeV Cl, 5×10^{14}
Au on W	20 MeV Cl, 2×10^{14}